AD-A193 688 LASER STUDIES OF GAS PHASE RADICAL REACTION(U) OXFORD UNIV (ENGLAND) PHYSICAL CHEMISTRY LAB G HANCOCK 30 SEP 86 DAJA45-85-C-0034 1/1

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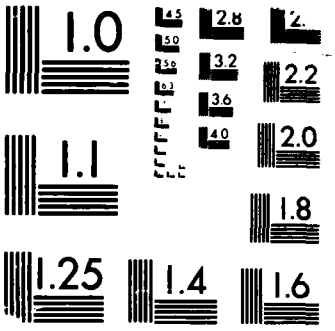

MICROCOPY RESOLUTION TEST CHART

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Laser Studies of Gas Phase Radical Reaction

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2nd & 3rd Periodic Report

1 April 1986 - 30 September 1986

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Report

1. Laser induced fluorescence of the CF radical

Preliminary LIF studies of CF are now almost complete. High quality spectra have been obtained, rotational constants of the $A^2\Gamma^+$ state have been refined, and lifetime studies are nearing completion.

2. The O + CHF reaction

Infrared emission from the reaction

$$O + CHF \rightleftharpoons \text{products}$$

has been observed, although the weakness of the signal has prevented wavelength resolved measurements through a monochromator from being carried out. The CHF radical was formed by pulsed laser irradiation, and the kinetic behaviour of the total emission has been studied as a function of both oxygen atom and CH_2F_2 radical precursor concentrations. It appears that the relatively high precursor pressures needed to observe emission are complicating the reaction scheme expected from previous studies of the vacuum uv emission accompanying this reaction. We are starting experiments using a range of ir filters in order to identify the emitting species.

Research plans for the remainder of the contract are:

(i) to pursue investigations of O + CHF and N + CHF reactions : most of the data for the former are now complete.

(ii) to attempt measurements of CF kinetics now that we have established the laser induced fluorescence spectrum.

(iii) to look for the FCO radical in laser induced fluorescence and to study its kinetics.

These are substantially as outlined in the research proposal.

2. The O + CHF and O + CF_2 reactions

Infrared emission from both reactions has been observed. The O + CHF reaction is kinetically very complex, but evidence supports vibrationally excited CO as being the main emitter, and quenching rate constants for this species have been measured. The O + CF_2 reaction appears kinetically simpler. Two components of ir emission have been identified and are consistent with FCO and CO formation being major and minor channels respectively in the reaction.

In both cases wavelength resolved emission was too weak to be observed with our existing monochromator. We are now constructing an interferometer detection system, and will use pulsed Fourier transform methods to extract the time and wavelength resolved ir signals.

Laser induced fluorescence of FCO has been seen (in a completely different reaction system) in some unpublished experiments at the Max Planck Institute in Gottingen. We now have the wavelength information to allow us to search for the radical : our initial efforts were at too high a laser frequency.

3. Publications

Two Part II theses (reports on full time research projects carried out over a nine month period by fourth year Chemistry undergraduates) have been produced on the work outlined in sections 1 and 2. It is hoped that a publication on our CF and CCl laser induced fluorescence work will be completed shortly.

4. Personnel

One full time graduate student is now working on the project, and one Part II student will be spending part of her research time on the project. In addition, Professor J.B. Halpern from Howard University, Washington DC has joined the group from July 1986 on sabbatical leave for a full year. He wishes to work in the kinetics side of our research and on problems outlined in this research proposal. I feel that this will bring valuable expertise into the project, and will greatly assist in its success. Consequently, from within the agreed budget for the project, Professor Halpern is being paid expenses of $1000 per month, and this will be either for a maximum of ten months or for a period of six months, the latter condition applying if a proposal to the SERC for a visiting fellowship for Professor Halpern for the period January - July 1987 is successful. I have spoken with Dr. D. Squire about this change in the utilisation of funds and he has suggested that this change should be noted in the periodic report.

Professor Halpern's involvement allows us to try an additional kinetic experiment involving quantum state resolved measurements in chemical reactions. This involves measurements of the nascent rotational state distribution in the CO product of the reaction

$$O + CS \longrightarrow CO + S$$

High population inversions on CO vibrational states are known, and a rotational distribution would enable comparisons of the quantum states produced and expected from simple trajectory calculation on a model potential surface. An existing (and unused) apparatus has been modified for this experiment : Professor Halpern is currently testing the detection system on a more simple

problem, the detection of OH from the two photon dissociation of H_2O using the same laser system as for the O + CS experiment. These new studies, on measurements of detailed rates of chemical processes into quantum states of products, are entirely within the spirit of the initial proposal, 'Laser Studies of Gas Phase Radical Reactions', and I believe that Professor Halpern's involvement in both these and the $CF/CHF/CF_2$ kinetics experiments during this year will benefit the research project greatly.

Research plans for the remainder of the contract are

i) to observe time and wavelength resolved ir emissions from the O + CHF and O + CF_2 reactions, and to extend these to the N + CHF system

ii) to attempt CF kinetic measurements

iii) to observe FCO laser induced fluorescence and to start kinetic measurements on the radical

iv) to measure quantum state distributions on the O + CS reaction

These are substantially as outlined in the research proposal.

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